Environmental Pollution 240 (2018) 353–358

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Lidar mapping of atmospheric atomic mercury in the Wanshan area, China☆

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ARTICLE INFO

Article history:
Received 11 January 2018
Received in revised form
26 March 2018
Accepted 23 April 2018

Keywords:
Differential absorption lidar
Wanshan
Gaseous atomic mercury
Concentration mapping

ABSTRACT

A novel mobile laser radar system was used for mapping gaseous atomic mercury (Hg^0) atmospheric pollution in the Wanshan district, south of Tongren City, Guizhou Province, China. This area is heavily impacted by legacy mercury from now abandoned mining activities. Differential absorption lidar measurements were supplemented by localized point monitoring using a Lumex RA-915M Zeeman modulation mercury analyzer. Range-resolved concentration measurements in different directions were performed. Concentrations in the lower atmospheric layers often exceeded levels of 100 ng/m^3 for March conditions with temperature ranging from 5 °C to 20 °C. A flux measurement of Hg^0 over a vertical cross section of 0.12 km^2 resulted in about 29 g/h. Vertical lidar sounding at night revealed quickly falling Hg^0 concentrations with height. This is the first lidar mapping demonstration in a heavily mercury-polluted area in China, illustrating the lidar potential in complementing point monitors.

1. Introduction

Mercury is a neurotoxic heavy metal pollutant. Metallic mercury has a high vapor pressure and, in the atmosphere, it largely remains in gaseous atomic form (Hg^0) and can spread easily through air transportation (Beckers and Rinklebe, 2017; Mazzolai et al., 2004; Rinklebe et al., 2010). Mercury is now the target of the UN's Minamata Convention legally entered into force in 2017 (United Nations, 2013). China, one of the signatory countries, is a major producer and user of mercury and much attention is paid to its study and mitigation in the environment (Feng, 2005; Feng and Qiu, 2008; Fu et al., 2012; Streets et al., 2005; Zhang and Wong, 2007). The mercury emissions of anthropogenic origin in China are estimated to be more than 500 tons annually (Streets et al., 2005). The Guizhou province is rich in mercury minerals, and mining activities in the Wanshan area of Eastern Guizhou have been ongoing since the Qin Dynasty, about 200 BC. Known as the Chinese mercury capital, Wanshan was the largest mercury mine in China up till the official close-down of the activities in 2002. However, some non-official artisanal activities have been ongoing since then, causing a substantial detrimental environmental impact. The study of mercury in the Wanshan area using point monitors has been extensive; see e.g. (Dai et al., 2012; Du et al., 2016; Feng et al., 2008; Li et al., 2009; Qiu et al., 2008).

The Wanshan mercury ore deposit is part of the global belt of cinnabar (HgS) mineralization, which has a large extension. In Europe, Almaden (Spain), Abbadia San Salvatore (Italy) and Idrija (Slovenia) are sites of historically major mercury extraction. The fact that atmospheric mercury is largely in atomic form while all other gaseous pollutants are molecular results in a unique possibility for extremely sensitive optical mercury detection, down to the Northern hemispherical background concentration in the range 1.3–1.6 ng/m^3 (Sprovieri et al., 2016). Then the differential absorption lidar (DIAL) technique becomes very useful for range-resolved concentration measurements (Svanberg, 1994).

☆ This paper has been recommended for acceptance by Dr. Jorg Rinklebe.

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https://doi.org/10.1016/j.envpol.2018.04.104
0269-7491/

The lidar group of Lund University, Sweden, has performed extensive studies on atmospheric Hg^0. The total flux from the electrolytic cell houses of chlor-alkali industries, where Hg^0 is used as an electrode in the electrolytic baths producing sodium hydroxide, has been determined (Grönlund et al., 2004, 2005b). Further, the mapping of Hg^0 in Icelandic and Italian thermal fields has been pursued (Edner et al., 1991, 1992). As part of a larger program of studies of gases of geophysical origin (Svanberg, 2002), lidar mapping of atomic mercury at all major European mercury mines was performed (Edner et al., 1993; Ferrara et al., 1998; Grönlund et al., 2005a).

DIAL is widely used in the measurement of various kinds of gases, including O_3, CO_2, and CH_4 (Burlakov et al., 2010; Innocenti et al., 2017; Koch et al., 2004). However, the measurement of gaseous atomic mercury requires very specialized equipment and had only been pursued by the Lund university group. With the cessation of this research direction in Lund, the South China Normal University group is now the only group world-wide which can perform such measurement. Along these lines, the present paper now reports the first DIAL study of Hg^0 in a heavily mercury-polluted area in China. The demonstration shows the substantial potential of this technology in complementing customary point monitoring studies and could provide a new dimension in the management of the serious mercury pollution in certain areas of Asia.

2. Mobile lidar system description

An advanced mobile lidar system has just been constructed at South China Normal University, Guangzhou with the prime purpose of atomic mercury monitoring on the Chinese scene (Zhao et al., 2017). The measurements of atmospheric Hg^0 in the Wanshan mining area reported here were conducted using this system, which is shown in photographs in Fig. 1 on a site close to the Wanshan city center (27° 31′ 23.0″ N, 109° 12′ 41.3″ E). This location was chosen because of being in the residential area where the population is subjected to the pollution, and because of the convenient availability of three-phase electrical power.

A detailed description of the system can be found in (Zhao et al., 2017). Here only a brief overview of the system is given. Equipped with a Nd:YAG laser, the system can emit laser radiation at a pulse repetition rate of 20 Hz at the primary wavelength of 1064 nm, with harmonics at 532 nm, 355 nm and 266 nm as generated in phase-matched non-linear crystals. When pumping the tunable dye laser supplied with the system, intense pulses of a wide range of wavelengths can be obtained. In particular, about 10 mJ/pulse of radiation at the atomic mercury absorption line close to 253.7 nm can be attained by frequency doubling of the dye laser radiation generated when using the dye Coumarin 307. A 40-cm–diameter receiving Newtonian telescope is used to collect back-scattered radiation. A stepping motor-driven roof-top mirror is used for deflecting the vertically transmitted beam and the field of view of the co-axially arranged telescope, allowing the direction of measurement to be changed 360° horizontally and the elevation angle to be adjusted between −10° and 45°.

Using a piezo-electric fast-wavelength switching arrangement, the wavelength could for every other transmitted pulse be changed from the Hg^0 absorption line to an adjacent non-absorbed wavelength, while avoiding the influence of near-by molecular oxygen lines, as discussed in (Mei et al., 2014). Signals in the form of lidar transients for the two wavelengths could then be digitized and averaged over many laser pulses to attain the necessary signal-to-noise ratio, to allow a range-resolved concentration evaluation from the ratio curve (Svanberg, 1994). The attainable range is limited by the $1/R^2$ signal fall-off for lidars operating in back-scattering mode. The whole system, including the setting of measurement directions, is controlled in LabVIEW software installed in the system computers, which also visualize the signal collected. A quasi–real-time data evaluation program is developed in MATLAB. In our data evaluation, an atomic mercury differential absorption cross-section of $2.5*10^{-14}$ cm^2/atom was adopted, as discussed in Mei et al. (2014).

3. Measurements and results

3.1. Introduction to the measurements

Fig. 2 is an overview of the measurement area. The mobile system was parked approximately, 600 m west of the border to the National Mining Park of Wanshan, which is the site of abandoned ancient mercury mines. Differential absorption lidar recordings are illustrated in Fig. 3 which were obtained from measurement direction A as indicated in Fig. 2 (a) and with an elevation angle of about 20°. In Fig. 3 (a), a pair of on- and off-resonance lidar recordings is shown with different scales at different distances, (b) shows the on/off ratio (DIAL) curve and the correspondingly evaluated concentration. Identical on/off curves, resulting in a constant ratio of 1.00, would correspond to the complete absence of absorbing Hg^0. Instead, the curve in (b) is clearly sloping with different inclinations, from which the range-resolved atomic mercury concentration is evaluated. Fluctuating and frequently very high Hg^0 concentrations were observed in this heavily polluted area.

Although the typical detection distance of our system for Hg^0 is roughly 1 km, reliable data obtained in the Wanshan area normally were available only out to a distance of about 700 m. One reason is the heavy absorption of the on-resonance lidar curve due to the exceedingly high concentrations in the local atmosphere. We further by routine reject the data recorded from ranges shorter than 100 or 150 m, since they may be compromised by the very high

Fig. 1. The South China Normal University mobile system operating on site in Wanshan for monitoring of atmospheric atomic mercury.